

## IRRADIATION EFFECTS ON THE OPTICAL PROPERTIES OF a-Ge-Se-Ag THIN FILMS

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The present paper reports the effect of proton irradiation on the optical properties of  $(\text{Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$  thin film. It has been observed that the proton irradiation changes the refractive index ( $n$ ) and the oscillator strength ( $E_d$ ). The data on the dispersion of the refractive index,  $n(\lambda)$  have been calculated using the single-effective-oscillator model. We have observed an increase in  $E_d$ , static refractive index  $n(0)$ , coordination number of the cation nearest neighbour of the anion  $N_c$ . Oscillator energy  $E_0$  decreases after the proton irradiation which indicate a decrease in the disorder of a- $(\text{Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$  glassy alloy. The absorption coefficient ( $\alpha$ ) has been calculated. The optical gap ( $E_g^{\text{opt}}$ ) and disorder parameter ( $B^{1/2}$ ) have been calculated from the intersection of the plot  $(\alpha\hbar\omega)^{1/2}$  vs.  $\hbar\omega$  with the abscissa axis and the slope of the plots. The values of  $E_g^{\text{opt}}$  and  $B^{1/2}$  decrease after proton irradiation. Results have been explained in terms of the structural changes due to the phase separation in thin films which are induced after the proton irradiation.

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### 1. Introduction

Non-oxide, chalcogenide glasses are of interest for application in infrared technology, including the fabrication of optical elements such as mirrors and filters [1-4]. The low characteristic vibrational frequencies of chalcogenide bonds allow them to transmit far out into the infrared [5]. These glasses show a variety of photo-stimulated phenomena when exposed to light or other radiations [6,7]. When these glasses are irradiated with high energy particles or light, bond breaking and bond rearrangement can take place, resulting in the change in local structure of these materials. These include subtle effects such as shifts in the absorption edge (photo-bleaching and photo-darkening), and more substantial atomic and molecular reconfiguration such as photo-induced refractive index changes and photo-doping effects [8]. In general, these phenomena are associated with the changes in the optical constants [9] and absorption edge shift [6], allowing the use of these materials in the fabrication of a large number of optical devices. This clearly underlines the importance of these glassy materials by accurate determination of their optical constants, refractive index and extinction coefficient and the optical band gap.

The dominant feature of Ge-Se glassy network is fourfold coordinated Ge and its structure is a function of composition [11]. Various physical properties of these glasses show a discontinuity at a composition when the average coordination number  $\langle r \rangle = 2.4$ . Coordination number of Ge is 4 and Se is 2, so at  $x = 20$ , the value of  $\langle r \rangle = 2.4$  in a- $\text{Ge}_x\text{Se}_{100-x}$  system. In the Se rich zone, the structure consists of Se chains linked by Ge atoms tetrahedrally coordinated by Se atoms i.e. the structure consists of chains of corner shared  $\text{GeSe}_{4/2}$ . As the Ge concentration increases the corner shared tetrahedrons give place to edge shared ones [11]. It has been reported that at a concentration about 20 at. % of Ge, a new non-crystalline compound  $\text{GeSe}_4$  exists in the Ge-Se system [12]. It has been

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seen that the addition of Ag has dual chemical role as an additive in Ge-Se chalcogenide glasses [13,14]. In Se-rich compositions ( $x < 1/3$ ), Ag acts as a network modifier and phase separates into  $\text{Ag}_2\text{Se}$ -rich glass, leaving the  $\text{Ge}_t\text{Se}_{1-t}$  backbone Se deficient ( $t > x$ ). However, in Ge rich compositions ( $x \geq 2/5$ ), Ag becomes a network former. As a network modifier, a bimodal glass transition temperature ( $T_g$ ) is reported and attributed to a phase separation of Ag centered structures (resembling  $\alpha\text{-Ag}_2\text{Se}$ ) from the host matrix [13,14].

The aim of the present paper is to see the effect of proton ion irradiation on the optical properties of such a technically important material i.e.  $a\text{-(Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$  thin films. In this paper, a relative simple method [15,16] for determining the optical constants has been used. Optical transmission spectra have been taken in the wavelength range 400–2000 nm. The optical parameters like refractive index ( $n$ ), absorption coefficient ( $\alpha$ ), oscillator strength ( $E_d$ ), oscillator energy ( $E_0$ ) and optical gap ( $E_g$ ) have been calculated. The effect of proton irradiation has been studied on these optical parameters. It has been observed that these parameters change after the proton irradiations.

## 2. Experimental procedure

Glassy alloy of  $a\text{-(Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$  has been prepared by quenching technique as described elsewhere [17]. Thin films of the alloy is prepared by vacuum evaporation technique on well-degassed Corning 7059 glass substrates at room temperature and base pressure of  $\sim 2 \times 10^{-5}$  mbar using a molybdenum boat. Amorphous nature of the films is confirmed by the absence of any sharp peak in the X-ray diffractograms of the films.

The samples are irradiated at room temperature in vacuum ( $\sim 10^{-6}$  Torr), using  $1 \times 10^{15}$  ions/cm<sup>2</sup> at 3 MeV proton energy from Chandigarh Cyclotron. The beam was focused using a circular collimator so that an area of  $\sim 0.75$  cm<sup>2</sup> on the films received a uniform ion dose. The normal incidence transmission spectra of the substrate with and without  $a\text{-(Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$  thin film have been measured by a double beam UV/VIS/NIR computer controlled spectrophotometer [Hitachi-330], in the transmission range 400–2000 nm. The spectrophotometer was set with a suitable slit width of 1 nm, in the spectral range. All optical measurements have been performed at room temperature (300 K).

## 3. Results and discussion

The model behind Swanepoel's method [15,16] assumes that the sample is a thin film of non-uniform thickness deposited on a transparent substrate having a refractive index ( $s$ ). The system is surrounded by the air, whose refractive index is  $n_0 = 1$  as shown in Fig. 1.

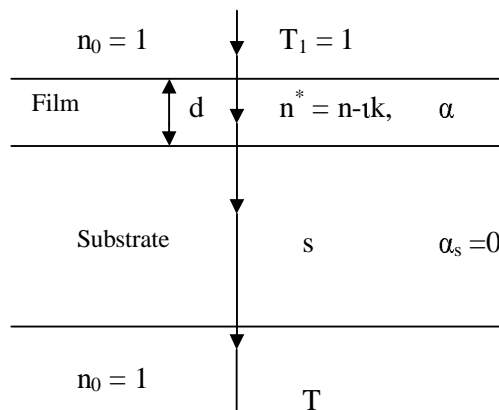


Fig. 1. System of an absorbing thin film on a thick finite transparent substrate.

The film has a complex refractive index  $n^* = n - ik$ , where  $n$  is the refractive index and  $k$  the extinction coefficient. The refractive index in the region where the absorption coefficient,  $\alpha \approx 0$  is calculated by equation [15]

$$n = \sqrt{N + \sqrt{N^2 - S^2}} \quad (1)$$

where

$$N = 2s \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}} + \frac{s^2 + 1}{2} \quad (2)$$

$T_{\max}$  and  $T_{\min}$  are the envelope values at the wavelengths in which the upper and lower envelopes and the experimental transmission spectrum are tangent respectively, as shown in Fig. 2. The accuracy in  $\lambda$  measurements is  $\pm 1$  nm. Fig. 2 shows the normal incidence optical transmission spectra of a-(Ge<sub>20</sub>Se<sub>80</sub>)<sub>0.96</sub>Ag<sub>0.04</sub> thin film before and after proton irradiation. The envelopes of the transmission spectrum,  $T_{\max}$  and  $T_{\min}$  have been observed from this figure. Using equation (1), the values of  $n$  are calculated at wavelengths corresponding to the tangent points. If  $n_1$  and  $n_2$  are the refractive indices at two adjacent tangent points at  $\lambda_1$  and  $\lambda_2$ , then according to the basic equation for interference fringes:

$$2nt = m\lambda \quad (3)$$

where  $m$  is an order number.

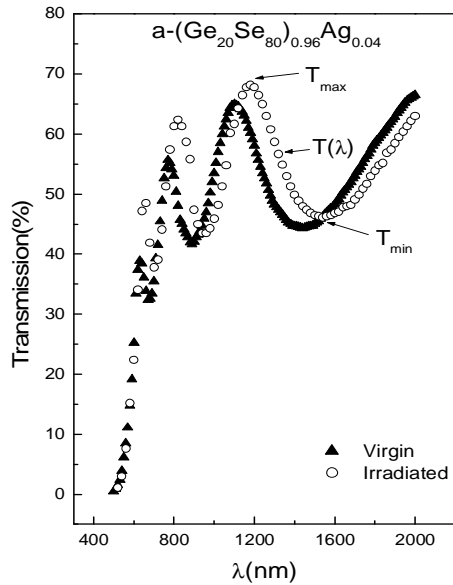


Fig. 2. Optical transmission spectrum for a-(Ge<sub>20</sub>Se<sub>80</sub>)<sub>0.96</sub>Ag<sub>0.04</sub> thin film before and after irradiation.

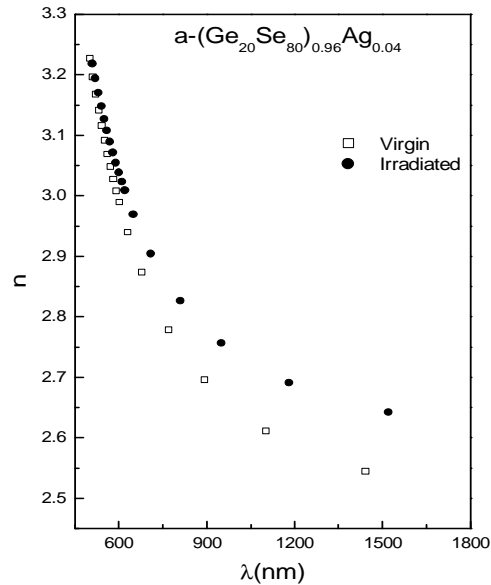


Fig. 3. Variation of  $n$  with wavelength ( $\lambda$ ) in virgin and irradiated state.

The thickness ( $t$ ) is given by

$$t = \frac{\lambda_1 \lambda_2}{4(\lambda_1 n_2 - \lambda_2 n_1)} \quad (4)$$

Using equation (3), new more precise values of the refractive index and the film thickness were determined by a procedure which was explained in detail in [15,16]. The calculated values of refractive index at different wavelengths have been plotted in Fig. 3. The data on the dispersion of the refractive index,  $n(\lambda)$  have been calculated using the single-effective-oscillator model proposed by Wemple and DiDomenico [18,19]. They found that all the data can be described to an excellent approximation by the following relation:

$$n^2(\hbar\omega) = 1 + \frac{E_d E_0}{E_0^2 - (\hbar\omega)^2} \quad (5)$$

where  $\hbar\omega$  is the photon energy. Plotting  $(n^2 - 1)^{-1}$  vs.  $(\hbar\omega)^2$  allows us to determine the oscillator parameters, by fitting a linear function to the smaller energy data. Fig. 4 shows the plot of  $(n^2-1)^{-1}$  vs.  $(\hbar\omega)^2$ , which is a straight line.  $E_d$  and  $E_0$  can be directly determined from the slope,  $(E_d E_0)^{-1}$  and the intercept,  $E_0/E_d$ , on vertical axis. The values of  $E_0$ ,  $E_d$  and static refractive index,  $n(0)$  (i.e. extrapolated to  $\hbar\omega \rightarrow 0$ ) for this alloy thin film is similar to that of the other Se rich alloys reported in the literature [9,10]. After the proton irradiation, the values of  $n(0)$  and  $E_d$  increases from  $(2.531 \pm 0.004) - (2.629 \pm 0.004)$  and  $(18.9 \pm 0.01) - (20.8 \pm 0.01)$  eV respectively. The value of  $E_0$  decreases from  $(3.72 \pm 0.01) - (3.65 \pm 0.01)$  eV.

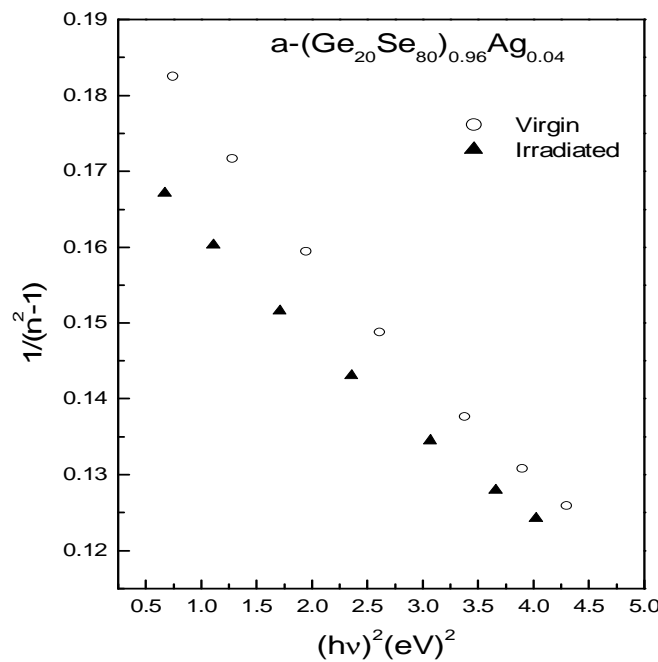


Fig. 4. Plot of  $1/(n^2 - 1)$  versus  $(\hbar\omega)^2$  in virgin and irradiated state.

The absorption coefficient ( $\alpha$ ) [20] can be calculated from the relation

$$x = \exp(-\alpha.t) \quad (6)$$

where  $x$  is absorbance as described elsewhere [15,16]. The calculated values of  $\alpha$  are plotted in Fig. 5. The absorption coefficient of amorphous semiconductors in the strong-absorption region ( $\alpha \geq 10^4 \text{ cm}^{-1}$ ), assuming parabolic valence- and conduction band edges, is given by [20]

$$\alpha(h\nu) = B(h\nu - E_g^{\text{opt}})^2 / (h\nu) \quad (7)$$

where  $E_g^{\text{opt}}$  is the energy distance between the valence and conduction band mobility edges. The parameter  $B$  given by the slope of the plots is an interesting parameter, since it can be taken as a measure of the disorder.

Finally, the optical gap ( $E_g^{\text{opt}}$ ) is calculated from the intersection of the plot  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  with the abscissa axis as shown in Fig. 6. The values of  $E_g^{\text{opt}}$  and  $B^{1/2}$  decrease from  $(1.85 \pm 0.01) - (1.81 \pm 0.01)$  eV and  $784 - 762 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$ , respectively.

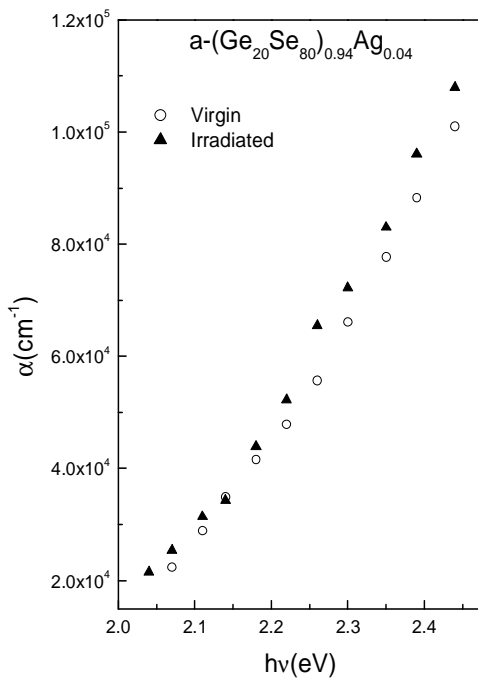


Fig. 5. Variation of absorption coefficient ( $\alpha$ ) with energy.

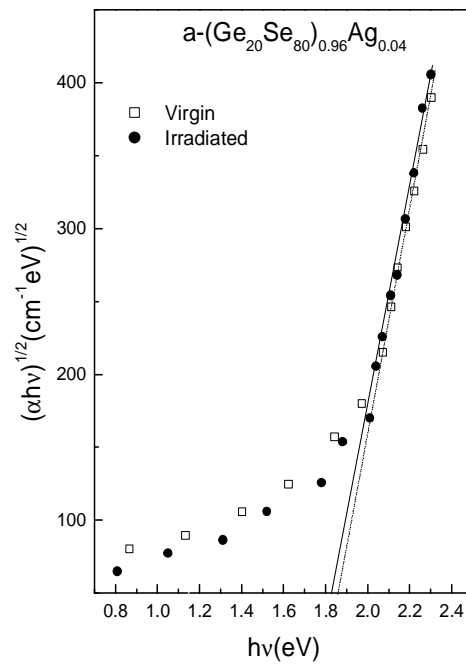


Fig. 6. Plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$ .

Amorphous  $\text{Ge}_{20}\text{Se}_{80}$  alloy has the structure of Se-Se bridges linked with  $\text{GeSe}_{4/2}$  edge-sharing units [12]. In Ge-Se-Ag system, interstitial voids are chemically ordered around the cation-centered structural units [ $\text{Ge}(\text{Se})_4$  tetrahedral]. Extrinsic atoms (Ag) are assumed to occupy these interstitial voids, thereby reducing the disorder in the system [21]. Dwivedi et al [22] have made the Raman measurements on 1 MeV  $\text{Kr}^{++}$  ion irradiated  $\text{a-Ge}_{21.5}\text{Se}_{78.5}$  thin films. They have observed that the band positions at  $201 \text{ cm}^{-1}$  [ $\text{Ge}(\text{Se})_{4/2}$  corner-sharing tetrahedral],  $215 \text{ cm}^{-1}$  [vibrations of Se atoms in the four member rings composed of two edge-sharing tetrahedral] and a band near  $263 \text{ cm}^{-1}$  [Se-Se bonds in Se chains]. Upon  $\text{Kr}^{++}$  irradiation, the intensity of the vibrational mode at  $263 \text{ cm}^{-1}$  related to Se-Se bonds in chains increases. Also, upon comparing the relative areas of the spectra, they found that upon irradiation, the relative area of band at  $201 \text{ cm}^{-1}$  is unchanged which indicates that the irradiation does not affect the number of  $\text{Ge}(\text{Se})_{4/2}$ . They have also shown that irradiation converts Se-Se bridges linked with [12] edge sharing  $\text{Ge}(\text{Se})_{4/2}$  units to Se-Se linear chains. The full width half maximum (FWHM) of the band at  $201 \text{ cm}^{-1}$  decreases after irradiation. The observed decrease in the width of this peak upon irradiation may mean a decrease in disorder. This decrease also indicates that irradiation increases ordering in the local structures [22].

Using the same arguments, we can explain the observed increase in the refractive index ( $n$ ) and the oscillator strength ( $E_d$ ). Upon irradiation in  $\text{a-(Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$  thin films with proton (3 MeV), Se-Se bridges linked with edge-sharing  $\text{GeSe}_{4/2}$  units, are converted into Se-Se linear chains. Ag may form the heteropolar bonds with these Se-Se chains. Upon irradiation, this material may

phase separates into an Ag<sub>2</sub>Se rich glass and decreasing the disorder in the material as suggested by Mitkova *et al.* [9]. In Se rich compositions, Ag acts as a network modifier and phase separates into an Ag<sub>2</sub>Se rich glass. They have made the Raman measurements on Se rich (Ge<sub>x</sub>Se<sub>1-x</sub>)<sub>1-y</sub>Ag<sub>y</sub> glassy system. Their Raman results suggest that Ag, present at triangular interstitial sites with coordination number (CN) = 3 in  $\alpha$ -Ag<sub>2</sub>Se, may be a good representation of the glass structure. Such a network will possess  $n_c = 3.33$  and from equation  $n_c = (5/2) r_m - 3$ , yield  $r_m = 2.53$ . Here the symbols  $n_c$  and  $r_m$  are known as mean constraints per atom and mechanical effective connectivity of the network. This value of  $r_m$  reside close to the critical connectivity ( $r_c$ ) = 2.40 to optimize the glass forming tendency within the constrain counting theory [23]. The decrease in the value of  $B^{1/2}$  from  $784 - 762 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$  also indicates that a decrease in the disorder of a-(Ge<sub>20</sub>Se<sub>100-x</sub>)<sub>100-x</sub>Ag<sub>0.04</sub> glassy system takes place after the proton irradiation.

The decrease of  $E_g^{\text{opt}}$  from  $(1.85 \pm 0.01) - (1.81 \pm 0.01) \text{ eV}$  is explained by the fact that the binding energy of the Ag-Ge bond ( $202.5 \text{ kJ mol}^{-1}$ ) is smaller than that of the Ge-Ge bonds ( $484 \text{ kJ mol}^{-1}$ ). Therefore, there is a smaller energy splitting between the states of the valence and conduction band takes place. In chalcogenide glasses, the lone pair orbital forms the valence band and the conduction band is formed by the antibonding orbital [24]. The proton irradiations excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger process that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process as suggested by Kamboj *et al.* [25]. In this process, bond breaking or ionization of atoms is easier to occur which leads to a change in the local structure of the amorphous network.

#### 4. Conclusions

Irradiation effects have been studied on the optical properties of a-(Ge<sub>20</sub>Se<sub>80</sub>)<sub>0.96</sub>Ag<sub>0.04</sub> thin film. After irradiation, the values of  $n$ ,  $E_d$  are increased and the value of  $E_0$  is decreased. The values of  $E_g^{\text{opt}}$  and  $B^{1/2}$  are also decreased after irradiation. The dispersion of the refractive index is explained in terms of the single oscillator model. The results have been explained in terms of the structural changes, which occur upon proton irradiation.

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